such a Cotton result be expected.[19,20] Accordingly the hydrogen on C-9 must have an axial (α) orientation in the ketone VI. Since none of the reactions and conversions from levopimaric acid should affect the geometry at C-9, this center must be α in the resin acid itself.

Experimental[21]

Hydroboration of Methyl Levopimarate.—A 300-ml., three-necked, round-bottomed flask was equipped with an addition funnel and a mechanical stirrer. The third neck was covered with a serum cap to permit removal of aliquots by means of a syringe. The system was flushed with dry nitrogen and cooled in an ice bath. Sodium borohydride (2.04 g., 0.054 mole) and a solution of 9.52 g. (0.132 mole) of 2-methyl-2-butene in 25 ml. of dry diglyme were placed in the cooled flask and a solution of 9.36 g. (0.066 mole) of boron trifluoride etherate in 25 ml. of dry diglyme was added, with stirring, over a period of 30 min. The mixture was allowed to stir for an additional 15 min. and then allowed to stand at ice temperature for 12 hr.

A solution of methyl levopimarate (prepared from 9.04 g. of levopimaric acid,[22] $[\alpha]^{16}\text{D}$ −252°, $\lambda_{\max}$ 272 mμ (ϵ 6500), by reaction with excess diazomethane) in 25 ml. of dry diglyme was added, at 0°, to the above reagent over a period of 45 min. The course of the reaction was followed by observing the disappearance of the maximum in the ultraviolet. After 5 days, about 50% of the diene had been consumed. At this time, an additional 33 mmoles of disiamylborane was added to the reaction mixture. At the end of 4 additional days the optical density in the ultraviolet had dropped to 10% of the original absorption.

To the reaction mixture there was added, slowly (frothing), 30 ml. of 3 *N* sodium hydroxide solution followed by the addition of 40 ml. of 30% hydrogen peroxide. The mixture was stirred at 0° for 1 hr. and then at room temperature for 2 hr. The reaction was diluted with water and the product extracted with benzene. The benzene solution was washed with water, acidic 5% ferrous sulfate solution, water, and then dried. The solvent was removed under reduced pressure and the white waxy product dried overnight at 70° (5 mm.), yield 10.0 g.

The crude product was chromatographed on 300 g. of activity III alumina. Elution with pentane separated diglyme and nonhydroxylated material. Elution with pentane–benzene (3:1 and 5:2) gave a total of 795 mg. of a minor alcohol. Pentane–benzene (2:1) yielded mixtures of two alcohols and elution with pentane–benzene (1:1), benzene, and benzene–ether (20:1) gave 4.79 g. of a major alcohol. Elution with ether yielded 200 mg. of a diol which was not examined further.

The major alcohol was recrystallized from methylcyclohexane, yield 4.01 g. (40%), m.p. 120–125°. This material was shown to be homogeneous by thin layer chromatography on silica gel (pentane–ether 1:1). An analytical sample was obtained by repeated crystallization from both methylcyclohexane and from methanol, m.p. 126.0–127.5°, $[\alpha]^{25}\text{D}$ +56° (c 1.49), $\epsilon_{205}^{\text{EtOH}}$ 10,000. Major peaks in the n.m.r. were found at τ 4.62, 6.08, and 6.34.

Anal. Calcd. for $C_{21}H_{34}O_3$ (334.48): C, 75.40; H, 10.25. Found: C, 75.45; H, 10.48.

The major alcohol was acetylated with acetic anhydride in pyridine and the crude product chromatographed on alumina. The acetate was recrystallized from aqueous methanol, m.p. 85.5–86.5°, $[\alpha]^{25}\text{D}$ +60° (c 2.00), $\epsilon_{205}^{\text{EtOH}}$ 9300. The n.m.r. spectrum showed peaks at τ 4.72, 5.08, 6.38, and 8.05.

Anal. Calcd. for $C_{23}H_{36}O_4$ (376.52): C, 73.36; H, 9.64. Found: C, 73.08; H, 9.52.

The minor alcohol was recrystallized from hexane and from aqueous methanol, m.p. 133.5–134.0 and 139.5–141.0°, $[\alpha]^{27}\text{D}$ −43° (c 1.88), $\epsilon_{205}^{\text{EtOH}}$ 9000. The major peaks in the n.m.r. were at τ 4.88, 6.30, and 6.71.

Anal. Calcd. for $C_{21}H_{34}O_3$ (334.48): C, 75.40; H, 10.25. Found: C, 75.66; H, 9.98.

Methyl 12-Keto-$\Delta^{8,14}$-dihydrolevopimarate.—To a solution of the major alcohol (402 mg., 1.2 mmoles, m.p. 120–125°) in 8 ml. of C.P. acetone cooled in an ice bath there was added 0.45 ml. (1.80 mmoles) of standard chromic acid–sulfuric acid solution (prepared from 26.7 g. of chromium trioxide and 23 ml. of concentrated sulfuric acid diluted to 100 ml. with water) over a period of 5 min. The mixture was allowed to stir for an additional 3 min. and then the reaction quenched with methanol. The mixture was diluted with water and extracted with ether The ether layer was washed, dried, and then evaporated to dryness to yield 348 mg. of solid yellow material. The compound crystallized well from either hexane or methanol but little if any purification was obtained as shown by the m.p. range of 123–135° and the presence of two spots on thin layer chromatography (silica gel, pentane–ether 1:1).

The crude material was chromatographed on 10 g. of Woelm activity III alumina. Elution with pentane–benzene mixtures and with pure benzene yielded 164 mg. (41%) of the β,γ-unsaturated ketone. There also was obtained about 50 mg. of more polar material but it was not examined. The unsaturated ketone is sensitive to air and should be isomerized immediately.

The β,γ-unsaturated ketone (164 mg.) was dissolved in 15 ml. of methanol, the solution flushed with nitrogen, sodium methoxide (75 mg.) added, and the solution allowed to stir for 5 hr. under a nitrogen atmosphere. The isomerization was followed by observing the development of a maximum at 238 mμ. The reaction was stopped by addition of 10% sulfuric acid, most of the methanol was removed under reduced pressure, and the product isolated by chloroform extraction. After evaporation of the chloroform the product was chromatographed on 5 g. of activity II alumina and the eluted material recrystallized from aqueous methanol, yield 48 mg. (12% from starting alcohol), m.p. 102.0–102.5°, $[\alpha]^{25}\text{D}$ +54° (c 1.15), $\lambda_{\max}^{\text{EtOH}}$ 238 mμ (ϵ 8800). The major n.m.r. bands were found at τ 3.78, 6.39, and 7.25.

Anal. Calcd. for $C_{21}H_{32}O_3$ (332.47): C, 75.86; H, 9.70. Found: C, 75.96; H, 9.78.

Methyl 12-Ketotetrahydrolevopimarate.—The α,β-unsaturated ketone (220 mg., 0.66 mmole) was hydrogenated in ethanol over prereduced platinum oxide (25 mg.) at atmospheric pressure. Theoretical hydrogen uptake was obtained in 90 min. The product was isolated in the usual manner and recrystallized from aqueous methanol, yield 114 mg. (51%), m.p. 98.5–99.5°, $[\alpha]^{27}\text{D}$ 11 ± 1° (c 1.27). The rotatory dispersion curve (c 0.106 in methanol) showed a peak at 311 mμ (amplitude +604°) and a trough at 269 mμ (amplitude −755°).

Anal. Calcd. for $C_{21}H_{34}O_3$ (334.48): C, 75.40; H, 10.25. Found: C, 75.06; H, 10.06.

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[19] R. H. Bible, Jr., and R. R. Burtner, *J. Org. Chem.*, **26**, 1174 (1961).

[20] Although the isopropyl group is probably equatorial, its configuration does not affect the predictions based on the Octant Rule.

[21] All melting points were taken in evacuated sealed capillaries and are uncorrected. Optical rotations were measured in chloroform. The n.m.r. spectral data are relative to tetramethylsilane as an internal standard. Chromatographies were performed of Woelm neutral alumina which had been deactivated to the desired activity by the addition of distilled water. All analyses were conducted by the Microanalytical Laboratory, College of Chemistry, University of California.

[22] The acid was obtained from *Pinus palustris* oleoresin (Sheldon Naval Stores Co., Valdosta, Ga.) by the procedure of Loeblich, Baldwin, O'Connor, and Lawrence (*J. Am. Chem. Soc.*, **77**, 6311 (1955)).

β-Bromocrotonolactone from the Bromination of Furoic Acid

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We wish to report the isolation, albeit in low yield, of β-bromocrotonolactone ($C_4H_3BrO_2$, m.p. 78°) from the bromination of furoic acid. The controversy[2a] regarding the early reports[3] (unconfirmed by later workers[4])

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[1] This work was carried out in the Department of Chemistry, Rice University, Houston, Tex.

[2] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953; (a) pp. 173–175; (b) pp. 118–121.

[3] (a) H. Limpricht, *Ann.*, **165**, 253 (1873); (b) H. H. Hodgson and R. R. Davies, *J. Chem. Soc.*, 806 (1939).

[4] P. S. Bailey and J. V. Waggoner, *J. Org. Chem.*, **15**, 159 (1950).

that the bromination of furoic acid produced an 84–85° melting $C_4H_3BrO_2$ compound has not been resolved. However, our first experiment provided a few crystals of a substance (m.p. 84°) whose infrared and ultraviolet spectra were identical to those observed for β-bromocrotonolactone which was isolated in all other experiments. This suggests that the higher melting product may be a polymorphic crystalline form of β-bromocrotonolactone.

Hodgson and Davies[3b] described their compound (m.p. 85°) as 2-bromo-3-hydroxyfuran and reported its reduction to an unauthenticated product, 3-hydroxyfuran. If 3-hydroxyfuran were actually the product, it would probably exist in its tautomeric keto form in accordance with results observed by Eugster and coworkers[5] regarding the keto–enol equilibrium of related compounds. Limpricht[3a] also reduced his bromo compound but did not obtain sufficient quantities to investigate the product. Only unidentified dark oils were produced when the reduction procedures of Hodgson and Davies[3b] were applied to β-bromocrotonolactone.

The identity of our 78° melting bromo compound was established by comparing its properties with those observed for an authentic sample of β-bromocrotonolactone prepared by hydrobromination of hydroxytetrolic acid.[6] The small coupling constant (J = 1.8 c.p.s.) between the α and γ-hydrogens observed in the n.m.r. spectrum[7] of β-bromocrotonolactone supports the previous assignment[2b,8] of the bromine to the β-position in this isomer. The α-hydrogen appeared as a triplet centered at 3.67 τ while the two γ-hydrogen gave rise to a doublet at 5.14 τ.

4-Bromo-2-furoic acid[4a,9] may be an intermediate in the conversion of furoic acid to β-bromocrotonolactone. Hill and Cornelison[10] demonstrated that the action of bromine water on 4-bromo-2-furoic acid produced β-bromocrotonolactone, while the isomeric α-bromocrotonolactone was formed from the treatment of 4,5-dibromo-2-furoic acid,[8a,9] with hydrobromic acid. The bromination of furoic acid may initially produce a small amount of 4-bromo-2-furoic acid which might be converted to β-bromocrotonolactone during the steam distillation.

In some experiments the crude products obtained from the bromination of furoic acid were not submitted to steam distillation but were worked up directly. In these instances bromofuroic acids corresponding to those reported by Bailey and Waggoner[4] were found.

Experimental

Bromination of 2-Furoic Acid.—Ten grams of furoic acid (m.p. 133°) was mixed with 10 ml. of water. Following Hodgson and Davies' procedure,[3b] the paste was stirred vigorously at 28–30° for 40 min. during the addition of 30 g. of bromine. After stirring the mixture for an additional 20 min., it was dissolved in 100 ml. of water and steam distilled. Extraction of the first 500 ml. of distillate with three 100-ml. portions of ether afforded, on evaporation, 340 mg. (3% yield) of β-bromocrotonolactone, m.p. 78°; $\lambda_{\max}^{H_2O}$ 224.5 mμ (ε 13,500); $\nu_{\max}^{CS_2}$ 1782, 1609, 1470, 1250, 1140. 1020, 860, and 758 cm.$^{-1}$.

The same product (m.p. 78°) was also obtained in low yield when the reaction was carried out by Hodgson and Davies' alternate procedure[3b] using chloroform as the reaction medium.

Our β-bromocrotonolactone showed no depression in melting point when mixed with a sample of β-bromocrotonolactone prepared by the method of Lespieau and Viguier[6] (see following); the β-anilino derivative[10] of our compound, m.p. 217–219°, agrees in melting point with that of the β-anilino derivative from the Lespieau and Viguier preparation (217–218° [10]; 220° [11]).

In the first experiment using the chloroform reaction medium a few crystals of an 84° melting substance were obtained from the ether extract of the steam distillate. This compound was characterized only by infrared (carbon disulfide) and ultraviolet (water) spectra which were identical in all respects to those observed later for β-bromocrotonolactone. Lack of material prevented further investigation of this compound.

When the product obtained from the bromination of furoic acid in water was not steam distilled but rather allowed to stand overnight in 100 ml. of water, crystals were obtained, m.p. 186–187°, corresponding to the 5-bromo-2-furoic acid (m.p. 186–187°) isolated by Bailey and Waggoner.[4] Similarly, the crude product from the bromination in the chloroform medium was dissolved in an ether–petroleum ether solution. On cooling this solution, a crystalline product (m.p. 158–160°) was obtained which corresponds to the 2,3,4,5-tetrabromotetrahydro-2-furoic acid (m.p. 159–160°) isolated by Bailey and Waggoner[4] from a similar reaction.

Attempts to Reduce β-Bromocrotonolactone.—β-Bromocrotonolactone was submitted to Hodgson and Davies' reduction procedure[3b] using 30% aqueous sodium hydroxide and 2.5% sodium amalgam and alternatively, sodium and ethyl alcohol. In both instances only a small amount of a dark brown oil, not characterized, was obtained.

β-Bromocrotonolactone from Hydroxytetrolic Acid.—Propargyl alcohol (16.8 g., b.p. 112–114°) was converted to hydroxytetrolic acid (13.3 g., m.p. 115–116°) by the procedure developed by Haynes and Jones[12] and modified by Henbest, Jones, and Walls.[13] Hydrobromination of hydroxytetrolic acid (10 g.) by Lespieau and Viguier's method[6] produced β-bromocrotonolactone (12.1 g.), m.p. 78°.

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[5] C. H. Eugster, R. E. Rosenkranz, K. Allner, and A. Hofmann, *Angew. Chem.*, **73**, 737 (1961).

[6] R. Lespieau and P. L. Viguier, *Compt. rend.*, **146**, 295 (1908); **148**, 419 (1909).

[7] For this n.m.r. spectrum the author is indebted to Dr. J. C. Davis, Jr., of the Department of Chemistry, University of Texas. The spectrum was taken in dueteriochloroform on the Varian HR-60 spectrometer using tetramethylsilane as an internal reference.

[8] The controversy regarding the position of the bromine in the two isomeric bromocrotonolactones (m.p. 58° and m.p. 78°) was clarified by (a) R. J. Vander Wal, *Iowa State Coll. J. of Sc.*, **11**, 128 (1936–37) [*Chem. Abstr.*, **31**, 2207 (1937)]; (b) M. C. Whiting, *J. Am. Chem. Soc.*, **71**, 2946 (1949); (c) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3105 (1949); (d) K. Sukigara, Y. Hata, Y. Kurita, and M. Kubo, *Tetrahedron*, **4**, 337 (1958); (e) Y. Hata, S. Senoh, and M. Murakami, *Nippon Kagahu Zasshi*, **79**, 1531 (1958) [*Chem. Abstr.*, **54**, 24620 (1960)]; (f) M. Murakami, S. Senoh, and Y. Hata, *Mem. Inst. Sci., Ind. Res. Osaka Univ.*, **16**, 219 (1959) [*Chem. Abstr.*, **54**, 22555 (1960)].

[9] The question relating to the position of the bromine in these substituted furoic acids was resolved by: (a) H. Gilman and G. F. Wright, *Chem. Rev.*, **11**, 323 (1932); (b) H. Gilman, R. J. Vander Wal, R. A. Franz, and E. V. Brown, *J. Am. Chem. Soc.*, **57**, 1146 (1935).

[10] H. B. Hill and R. W. Cornelison, *Am. Chem. J.*, **16**, 188, 277 (1894).

[11] L. Wolff and W. Schimpff, *Ann.*, **315**, 151 (1901).

[12] L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 503 (1946).

[13] H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *ibid.*, 3646 (1950).

Triethylsilyltriethylgermane[1]

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We wish to report the synthesis and some properties of triethylsilyltriethylgermane which appears to be the

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